Preparation and Some Physical Properties of Sulphur Tetrafluoride.

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Previous work on sulphur tetrafluoride is summarised. A reliable, if somewhat tedious, method for its preparation from the elements and its subsequent purification are described. Its melting and boiling point, density, surface tension, and vapour pressure have been determined. These data are shown in relation to the properties of the tetrafluorides of selenium and tellurium.

Besides sulphur hexafluoride and disulphur decafluoride, three others, collectively referred to as lower fluorides—tetrafluoride, difluoride, and disulphur difluoride—are mentioned in the literature. Some or all of the latter are formed in most of the reactions where the hexafluoride, or its first homologue, is the main product. Invariably these lower fluorides accompany one another when the aim is to produce any one of them. According to Trautz and Ehrmann (*J. prakt. Chem.*, 1935, **142**, 79) disulphur difluoride readily decomposes to sulphur difluoride, though Dubnikoff and Zorin (*J. Gen. Chem., U.S.S.R.*, 1947, **17**, 185), who made it by the action of excess of sulphur on silver fluoride at 200°, say that decomposition takes place above that temperature. We are inclined to think, with Trautz and Ehrmann (*loc. cit.*), that neither of these fluorides has yet been obtained pure, although a m. p., −105·5°, and b. p., −99°, have been reported for disulphur difluoride (Centnerszwer and Strenk, *Ber.*, 1925, **58**, 814).

The present communication deals with sulphur tetrafluoride; as the compound has been so recently described as "almost certainly wrong" (Sidgwick, "The Chemical Elements and their Compounds," Oxford, 1950, Vol. II, p. 943), a brief review of the facts is not inappropriate. Ruff and Thiel (*Ber.*, 1905, **38**, 549) failed to get it by the action of hydrogen fluoride with sulphur nitride or tetrachloride, or of the latter with titanic or stannic fluoride, or arsenic trifluoride, but Ruff and Heinzelmann (*Z. anorg. Chem.*, 1911, **72**, 63) appear, from the properties they reported, to have had a material which contained some tetrafluoride, but they do not seem to have recognised its presence. Heating sulphur with mercury fluorides (Ruff and Bahlau, *Ber.*, 1918, **51**, 1752), iodine heptafluoride (Ruff and Keim, *Z. anorg. Chem.*, 1930, **193**, 176), or fluorine (Schumb and Gamble, *J. Amer. Chem. Soc.*, 1930, **52**, 4302; Yost and Claussen, *ibid.*, 1933, **55**, 885; Denbigh and Whytlaw-Gray, *J.*, 1934, 1347) gave unidentified lower fluorides. Examination of the gaseous product of the reduction of cobalt trifluoride with sulphur by Fischer and Jaenckner (*Z. angew. Chem.*, 1929, **42**, 810) led them to believe it was the tetrafluoride. Their results were not reproducible; and, later, Luchsinger (Diss., Breslau, 1936) showed that the metal fluorides when heated with sulphur produce mixtures of all the above-named fluorides of sulphur in proportions depending on the kind of fluoride, the ratio of fluoride to sulphur used, and the rate at which the reaction proceeds. Silvey and Cady (*J. Amer. Chem. Soc.*, 1950, **72**, 3624) separated the tetrafluoride from the breakdown products of $CF_3{\cdot}SF_5$ in a high-voltage discharge (Linn and Geballe, *J. Appl. Phys.*, 1950, **21**, 592). Disulphur decafluoride is decomposed by heat to a mixture of the hexa- and tetra-fluoride (Trost and McIntosh, *Canad. J. Chem.*, 1951, **29**, 508). Silvey and Cady (*J. Amer. Chem. Soc.*, 1952, **74**, 5792) and Tyczkowski and Bigelow (*ibid.*, 1953, **75**, 3523) both found the tetrafluoride present when carbon disulphide is mildly fluorinated with the element. Very recently, Schmidt (*Monatsh.*, 1954, **85**, 452) obtained a yellow solid on heating disulphur dibromide and iodine pentafluoride together in a steel bomb; this, when heated with copper turnings in a copper bomb, gave the tetrafluoride. Melting and boiling points of the materials believed to have been sulphur tetrafluoride, so far as reported, are set out with our own for comparison :

	m. p.	b. p.
1911, Ruff and Heinzelmann	−135°	−40°
1936, Luchsinger	−125·0	−40·0
1953, Tyczkowski and Bigelow	−122	−38
1955, Present work	−121·0	−40·4

In seeking a method giving uniquely the tetrafluoride, sulphides of silver, cadmium, cobalt, mercury, bismuth, zinc, and iron were treated with fluorine in various dilutions and at various temperatures. The solid solution of sulphur and iodine was also employed, and attempts were made to reduce iodine pentafluoride with sulphur. All these reactions gave sulphur hexafluoride with, in most cases, a little of what could be designated lower fluorides. The success or otherwise of an experiment was made manifest by the behaviour of the product : if the solid were allowed to sublime at atmospheric pressure, the amount of low-boiling liquid remaining proved a sure indication of the proportion of lower fluorides. Unfortunately, the proportions were so low as to render none of these methods worth pursuing, and we turned to a study of the fluorine–sulphur reaction. Enough had, however, been observed to make it clear that the working temperature was probably the most significant factor, and that, under any forseeable circumstance, a mixture containing some hexafluoride would be produced.

When fluorine and sulphur react the temperature can easily reach the point of inflammation, but even at much lower temperatures the major product is the highest fluoride. At about −150° the rate of reaction becomes impossibly slow and, according to our observations, is not productively useful below about −75°. To keep this optimum temperature in the reaction zone we tried a number of devices submerged in cooling baths : glass and metal columns packed with sulphur alone, and with nickel shot and sulphur ; flasks on the inner surface of which sulphur had been caused to set as a continuous coat ; flasks with a sublimate of sulphur on the inner surface. The columns, though sometimes as narrow as 0·5 in., invariably blocked up, either by reason of a partial melting of the sulphur particles, or through a deposit of sulphur from solution in the fluorides, or from the decomposition of disulphur difluoride. Its thermal conductivity is so low that a frozen layer of massive sulphur could not be effectively cooled, and the yield of lower fluorides proved small. Hence we turned to the method developed in this laboratory for the preparation of selenium tetrafluoride (*J.*, 1952, 1231), namely, the fluorination of sulphur in the form of a sublimate on a glass surface. In the case of selenium, almost pure tetrafluoride is produced when the temperature is kept about 0° ; for sulphur −75° is required, and the proportion of tetrafluoride is estimated at 40% of the total yield. We had found that the presence of moisture in any preparation invariably led to the formation of some thionyl fluoride, SOF_2, and sublimation of the sulphur in a vacuum proved a means of ensuring a sufficient drying of the element. Fluorine, largely diluted with nitrogen, was employed ; and the product, condensed by means of liquid oxygen, was subjected to a trap-to-trap distillation in a vacuum. There was some separation of sulphur either from solution or by the decomposition of disulphur difluoride at the later stages when the low-boiling head fraction containing hexa- and tetra-fluoride had been largely removed to leave a tail fraction consisting mainly of disulphur decafluoride (b. p. +29°). The former was split by fractionation in a Podbielniak column (*Ind. Eng. Chem.*, *Anal. Ed.*, 1931, **3**, 177 ; 1933, **5**, 119) working at something over two atm. pressure. After the removal of hexafluoride (b. p. −53°/2 atm.), a long refluxing was necessary to separate the thionyl fluoride, SOF_2 (b. p. −43·8°), from the tetrafluoride (b. p. −40·4°). The final product was characterised by measurement of vapour density and by determination of sulphur and fluorine. The almost complete freedom of the material from sulphur oxyfluorides and silicon tetrafluoride was shown by the infrared spectrum, and the Raman spectrum gave no evidence of these or of sulphur hexafluoride.

The following physical properties were determined, and Luchsinger's values, where available, are given in parenthesis :

Density (g. cm.$^{-3}$) at 200° K = 1·9191 (1·9333)
Density (g. cm.$^{-3}$) at T° K (170—200° K) = 2·5471 − 0·00314T (2·6253 − 0·00346T)
Coeff. of cu. expansion (c.c./c.c./°C) (170—200° K) = 0·00170
Melting point (° C) = −121·0° ± 0·5° (−125·0°)
Boiling point (° C) (from v.p.) = −40·4° (−40·1°)
Surface tension (dynes cm.$^{-1}$) at 200° K = 25·70
Surface tension (dynes cm.$^{-1}$) at T° K (190 — 230° K) = 61·36 − 0·1783T

Vapour pressure (mm.) at 200° K = 80·8 (120·6)
Vapour pressure (mm.) at T° K (160—224° K), log P = 8·8126 − 1381/T (7·7068 −1125·1/T)

The latent heat of vaporisation is 6320 cal. mole^{-1} and the Trouton's constant 27·1. From the relation $T_{\text{b.p.}}/T_c \sim 0{\cdot}67$ a critical temperature of 74° is indicated which is not far from the figure of 71°, the temperature at which the surface tension is zero. The relation between the tetrafluorides of sulphur and selenium (values mainly from Peacock, *J.*, 1953, 3617) is shown below and it may be noted that Trouton's constant is high in both cases, suggesting some association.

	SF_4	SeF_4
Melting point (° C)	−121°	9·5°
Boiling point (° C)	−40·4°	106°
Approx. critical temp. (° C)	70°	290°
Trouton's constant	27·1	30·0
Molar latent heat of vaporisation (cal.)	6,320	11,240
Surface tension at b. p. (dynes cm.$^{-1}$)	19·85	25·8

These data may be a guide to some of the physical properties of tellurium tetrafluoride, all of which, by reason of its attack on most materials, are difficult to ascertain. Earlier work in these laboratories indicated a melting point of a little over 100° and a boiling point about 250°. These are about the values that might be expected from the corresponding figures for the first two members of the series.

EXPERIMENTAL

Preparation.—After much exploratory work with various reactions we found the most promising to be that between fluorine and sulphur, and the most favourable conditions to be, the former well diluted with nitrogen, and the latter as a sublimate on a glass surface at −75°. The absence of oxygen and moisture is obligatory because thionyl fluoride is easily formed, either by a primary or secondary reaction, and is difficult to separate from the tetrafluoride. To meet these conditions an all-Pyrex glass train consisting of two conical flasks in series followed by a number of cylindrical traps and a break-seal vessel was used. This was well flamed under a vacuum with repeated fillings of oxygen-free nitrogen. Good quality sulphur, after being kept molten in a vacuum for some time to allow the release of moisture and gases, was deposited as a thin sublimate on the surfaces of the two conical flasks. Further to reduce the risk of introducing oxygen, the electrolytic fluorine cell was run for 2 hr. before the gas, after passing over sodium fluoride and being cooled to −180°, was used. The fluorine, at 850 c.c. per hr., diluted with 3 times its volume of nitrogen, previously freed from oxygen, dried over phosphoric oxide, and cooled to −180°, was passed through the train, the two flasks being submerged in ethanol–solid carbon dioxide at −75°, and the exit protected against ingress of moisture. The mild, low-temperature fluorination caused a colourless liquid to appear on the surface of the sulphur; most of this remained there and the rest was retained in the first trap beyond the reaction flasks, which was at −180°. At the end of a run, usually lasting 24 hr., the fluorine stream was stopped, and the flasks were allowed slowly to warm, with the nitrogen stream maintained; as a result the product containing 40% of sulphur tetrafluoride was all collected in the first trap. The reaction flasks were then sealed off and the rest of the train evacuated, the mixture of fluorides being kept frozen.

Purification.—The bulb-to-bulb vacuum-fractionation which followed, and during which a slight white deposit of sulphur appeared on the glass surfaces, was designed to remove as a tail fraction of about 2 c.c. most of the disulphur decafluoride (b. p. +29°). The rest of the material, about 22 c.c., was collected in a break-seal vessel for transference to the boiler of a Podbielniak still (*loc. cit.*). The column (67 cm. × 6 mm.) of the still was fitted with a metal spiral (5 turns per cm. of 24 s.w.g. wire) and surrounded by a sleeve-type, silvered vacuum-jacket. Liquid to provide the reflux was condensed by surrounding the head of the column with a small double-walled copper jacket which was cooled by blowing liquid air into the outer annulus whence it passed through the inner annulus to escape. The operating temperature was measured to ±0·5° by means of a calibrated base-metal thermocouple used in conjunction with a galvanometer. Since the material at this stage in the purification (except for the trace of silicon tetrafluoride still present) does not attack the metal, a mercury manometer reading to ~3 atm. was used for the pressure measurements. We found that the occasional, ordinary glass stopcock which greatly facilitated the operation of the column could be safely used up to this pressure, provided it was lubricated with hard fluorocarbon grease. As a precaution against its being blown out, the plug was secured by a stout rubber ring. Troublesome bumping was avoided by having a piece of capillary in the boiler.

Our practice, after the removal of sulphur hexafluoride had been signalled by a sharp rise in temperature at the still-head, was to reduce the pressure from 1800 to 800 mm. and, by a prolonged fractionation at this pressure, to get rid of the small amount of thionyl fluoride which was always present, and for which the oxygen is obtained from a slight attack on the glass mainly during preparation. In none of the distillations did we have any evidence of the presence of a second impurity at this stage, which led us to think that the amount of sulphur difluoride, if any, was small.

Characterisation.—Measurements of vapour density indicated a molecular weight of 108·8 ± 0·5 (SF_4 requires 108·1). For analysis a sample was dissolved by opening a bulb in a solution of 2·5% sodium hydroxide solution and 30% hydrogen peroxide; excess of the latter was destroyed by boiling, and the solution was made up to 100 c.c. An aliquot part was acidified and the sulphur determined as barium sulphate. A second aliquot part was passed through the cation-exchange resin, Zeo-Carb 225H, and the resulting aqueous solution of hydrogen fluoride and sulphuric acid was titrated hot with 0·1N-sodium hydroxide (Found: S, **30·36**; F, **69·11**. SF_4 requires S, 29·67; F, 70·33%).

Physical Properties.—Density was measured by observing the liquid level of a known weight of sulphur tetrafluoride (weighed as vapour; see *J.*, 1955, 2230, Fig. 1*a*) in the fine stem of a thermometer-type bulb, previously calibrated by means of mercury. The plot of density against absolute temperature is a straight line, of slope $-3{\cdot}14 \times 10^{-3}$.

Temp. (c)	−78·7°	−80·7°	−82·7°	−84·7°	−86·9°	−87·4°	−91·4°	−96·1°
(K)	194·5°	192·5°	190·5°	188·5°	186·3°	185·8°	181·8°	177·1°
Density (g./c.c.)	1·9358	1·9423	1·9377	1·9547	1·9618	1·9633	1·9777	1·9931
10^3 × Slope	−3·14	−3·14	−3·20	−3·14	−3·14	−3·14	−3·13	−3·13

The melting point was observed by noting the fall of a glass style through the melting solid (Stock, *Ber.*, 1917, **50**, 156) contained in a sealed vessel. This was submerged in a well-stirred bath of ether cooled with liquid nitrogen in a Dewar vessel, the temperature being measured by means of a copper–constantan thermocouple and a potentiometer. An accuracy of ± 0·5° is claimed.

Surface tension was measured by using two capillary tubes of different, known diameters mounted with the liquid in a sealed vessel (Mills and Robinson, *J.*, 1927, 1823). The apparatus was completely submerged in a low-temperature bath in an unsilvered Dewar flask through which the difference in capillary rise was observed by means of a cathetometer. An accuracy of ±0·2 dyne cm.$^{-1}$ is claimed; a plot against absolute temperature is a straight line, of slope 0·1783.

Temp. (c)	−76·8°	−64·7°	−57·2°	−50·0°	−45·5°
(K)	196·4°	208·5°	216·0°	223·2°	227·7°
Surface tension (dynes cm.$^{-1}$)	26·39	23·84	22·80	21·57	20·77
Slope	0·1781	(0·1800)	0·1785	0·1783	0·1783

Vapour pressure, as shown by preliminary work, is sensitive to impurity, whether this be the result of inadequate fractionation or from keeping the material too long in contact with glass. For this reason, sulphur tetrafluoride, specially purified, was used at once, with vacuum-transfer and rigorous drying of all apparatus. The container, a glass bulb, was directly attached to a mercury manometer, alongside which stood a barometer. The ether-bath fixing the temperature of the tetrafluoride was well stirred and kept to within ±0·1° of the required temperatures, a copper–constantan thermocouple and a potentiometer being used for the measurements. Besides calibration at fixed points, accuracy received a further check by observing the vapour pressures of ethylene, dichlorodifluoromethane, and trichlorofluoromethane between −130° and +10°. The heights of mercury in the manometer and barometer were read to ±0·02 mm. by means of a cathetometer. An accuracy of ±0·5 mm. is claimed for the vapour pressures.

Temperature		Pressure		
° c	° K	mm.	log	Slope
−112·3	160·9	1·56	0·1931	−1387
−102·7	170·5	5·14	0·7110	−1382
− 92·0	181·2	16·56	1·2191	−1376
− 83·6	189·6	36·78	5·5657	−1374
− 75·0	198·2	74·36	1·8714	−1376
−66·3	206·9	142·46	2·1538	−1378
−59·8	213·4	217·10	2·3367	−1382
−54·7	218·5	299·58	2·4766	−1385
−49·2	224·0	397·20	2·5990	−1392
			Mean	−1381

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